

The Fine Structure of the Near Infra-Red Absorption Bands of Water-Vapor

A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

BY

E. R. PHELPS

1925

In Arbor
1925



The Fine Structure of the Near Infra-Red Absorption Bands of Water-Vapor

A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

BY

E. R. PHELPS

1925

THE FINE STRUCTURE OF THE NEAR INFRA-RED ABSORPTION BANDS OF WATER-VAPOR

By E. R. PHELPS

ABSTRACT

With the advantage of better gratings it has become possible to extend previous studies of the absorption of radiation by water-vapor. The methods also represent a refinement of those previously employed, particularly in calibrating the spectrometer. The results of this study considerably enlarge our knowledge of the water spectra. Most important are measurements on the bands near $3.11\ \mu$ and $6.26\ \mu$.

The work recounted in the present paper is a further investigation of the absorption of near infra-red radiation by water-vapor. This study, begun by Langley,¹ has been continued by Paschen,² von Bahr,³ Sleator,⁴ Hettner,⁵ and others. The papers by von Bahr brought to light the surprising complexity of the absorption doublet described by Paschen near the wave-length $6\ \mu$. The bolographs and tables given by Sleator showed that von Bahr had by no means revealed the ultimate details of this absorption band. They proved also that the absorption found by Langley, near the wave-lengths $1.3\ \mu$, $1.8\ \mu$, and $2.6\ \mu$, was extremely, perhaps equally, complex. In neither of the four regions studied did Sleator complete the analysis, for while a few of the lines shown on his maps appear to be incapable of resolution by higher dispersion, more of them are still plainly combination effects. That is, one of them is not the graphical representation of the absorption of radiation of a single frequency. The spectrum of water, in short, is not yet as completely known as is the spectrum of hydrogen chloride by the work of Imes⁶ and Colby and Meyer.⁷ Since Sleator's paper was published, some improvements in

¹ S. P. Langley, "Researches on Solar Heat," *Professional Papers of the Signal Service*, No. 15, United States War Department, 1884.

² F. Paschen, *Annalen der Physik*, **51**, 4, 1894; **52**, 210, 1894; **53**, 234, 1894.

³ E. von Bahr, *Verhandlungen der deutschen Physikalischen Gesellschaft*, **15**, 731, 1913; *Philosophical Magazine*, **28**, 71, 1914. Other references concerning the history of the subject are given in the latter paper.

⁴ W. W. Sleator, *Astrophysical Journal*, **48**, 125, 1918.

⁵ G. Hettner, *Annalen der Physik*, **55**, 476, 1918.

⁶ E. S. Imes, *Astrophysical Journal*, **50**, 251, 1919.

⁷ W. F. Colby and C. F. Meyer, *ibid.*, **53**, 4, 1921.

apparatus and technique have made possible an increase in resolution in the near infra-red spectrum and a corresponding increase in our knowledge of the absorption spectrum of water-vapor.

The apparatus was the double spectrometer, with thermopile and galvanometer, employed by Sleator and by Imes. The improvement was due entirely to better gratings. These are echelettes ruled by Barker at the University of Michigan. They served so well in concentrating energy in particular spectra that the slits of the spectrometer could be made much narrower than before, and the spectral interval affecting the thermopile at a particular setting of the grating correspondingly decreased. Numerical values for this interval will be given in connection with the particular spectra described.

The present procedure in securing data is better than the method described by Sleator, for, in the first place, the spectrum line of mercury at wave-length 1.014μ was used in the calibration of some of the gratings. For others the band spectrum of hydrogen chloride near the wave-length 3.46μ , which has been mapped with precision by Colby and Meyer (*loc. cit.* on p. 28), served the same purpose. Eight or ten lines of the HCl spectrum were used for an average value of the spectrometer constant. Moreover the "zero reading" of the spectrometer, necessary in finding every value of the angle in the equation $\lambda = K \sin \theta$, was determined bolometrically in every case. This determination was made at the beginning or end of every observation period. It was customary also to check the calibration constant K by using the actual grating space G in the equation $\lambda = 2G \cos \phi/2 \sin \theta$. Certain chances of error in calibrating by visual means have thus been eliminated.

In securing one of the energy-curves for the region around 6μ , readings were taken at $\frac{1}{2}$ -minute intervals. For all the other curves, the standard interval was 1 minute, except where the complexity of the pattern demanded more minute examination. If one considers the spectrum as spread out on a surface in which the thermopile slit forms a hole, the step taken between readings produces a displacement of the spectrum about equal to the width of the slit. In general, six deflections of the galvanometer were recorded for each point plotted on an energy-curve. Figure 2 is a tracing of the larger part

of one of three independent curves, necessarily somewhat smoothed out in the process of reproduction, and, in its present form, unsuited to the actual determination of wave-lengths.

This paper contains the report of work on the absorption regions

TABLE I
WAVE-LENGTHS OF LINES IN THE ABSORPTION BAND AT 6.26μ . STARRED
VALUES WERE CHECKED, USING $\frac{1}{2}$ -MINUTE STEPS. μ IS THE UNIT

First Order	Second Order	Von Bahr	First Order	Second Order	Von Bahr
4.875			6.46	6.37	6.36
4.98	5.03	5.02		6.43	6.42
5.08	5.095	5.09			
	5.165	5.13	6.52	6.495	6.50
5.20	5.21	5.19		6.57	6.58
5.32	*5.295	5.27	6.615	6.62	
	*5.36	5.33		6.675	6.64
		5.40			
5.445	*5.42	5.44	6.72	6.72	6.72
	*5.475	5.50			
	*5.53	5.54		6.80	6.78
	*5.575	5.56	6.89	*6.875	6.87
5.60	*5.62	5.61		*6.92	6.91
	*5.65			6.975	6.97
5.69	*5.69	5.70	7.135	7.06	7.05
				7.165	7.17
	*5.74	5.74			
5.78	*5.77		7.29	7.21	7.22
	5.835	5.80		7.28	7.28
	5.88	5.86			
5.905	5.945	5.92	7.335	7.315	
	5.99	5.96		*7.39	7.36
6.09	6.065	6.04	7.475	*7.425	
	6.11	6.10		7.47	7.49
6.18	6.17	6.16	7.625	7.59	
	6.22			7.805	
	6.28	6.28	8.025	7.94	

near 6.26μ , 3.11μ , 1.87μ , and 1.38μ , which will be taken up in order. It is convenient to speak of one of these regions as a band, but it does not seem certain that any one of them is a band in the sense of the word which is applied to the spectrum of hydrogen chloride.

Our first work in the important region at 6.26μ was done with an echelette grating having 480 lines per inch, using the first-order

spectrum. In the second order more absorption lines appeared, and the energy-curve was found to be very much like the one given by von Bahr (*loc. cit.* on p. 28), which was obtained with a prism. The two are given in Figure 1, and the corresponding wave-lengths in Table I. The probable error in these wave-lengths is 0.01μ or 0.02μ .

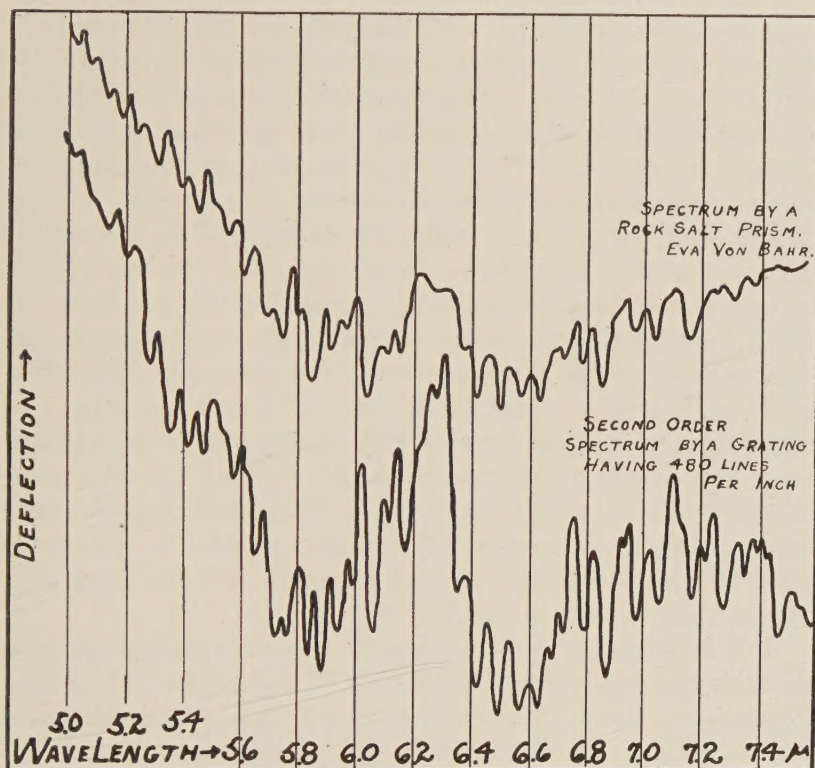


FIG. 1.—Water-vapor absorption near 6μ

The interest of Figure 1 arises from the good correspondence of the maps made with instruments of different types. The wave-lengths in Table I bear out the similarity, though of course they do not represent our most accurate work. From the figure given by von Bahr it seems that an interval of about $300 \text{ \AA}$ was included in the slit of the micrometer, or upon its receiving surface, and this is very nearly the value in the second-order grating spectrum under con-

sideration. Of course the significance of the number 300 Å depends upon the purity of the spectrum, though the numerical value is determined by dispersion, focal length of mirror, and slit widths. The graph in Figure 1 is a free-hand copy of the map appearing in von Bahr's paper, reversed to correspond with our own, and it does injustice to the details of the original.

A comparison of the data of Table I will convince the reader that the grating is a valuable instrument in the investigation of the spectral distribution of energy. Its primary advantage, however, lies in the high dispersion at its command. This advantage appears in Figure 2 and the data of Table II. Here the numbers presented were secured with another echelette having 2880 lines per inch. It was possible with this grating to work over the whole of the absorption region, of which Sleator had covered only about two-thirds, and immediately to identify and find wave-lengths for 107 lines, of which Sleator had given values for 59. In the first review of the region the slit of the thermopile was $\frac{1}{2}$ mm wide, and included a spectrum interval of about 80 Å. Finally, however, by using extreme care, the band was surveyed with the slits $\frac{1}{4}$ mm wide, readings being taken every half-minute of arc. In this way 126 lines were identified within the limits of the band. It appeared, however, that nearly all the new lines resulting from this re-examination were indicated by irregularities in the graph obtained with the wider slit, part of which appears in Figure 2.

It is interesting now to compare the wave-lengths appearing in this table with those given by Sleator (*loc. cit.* on p. 28) for the lines corresponding to the old numbers of column 2. In his paper the probable error in the wave-lengths of this region was put down as 20 Å. It appears, however, that there is a systematic variation between his values and our later ones, the average difference for the 59 lines tabulated being 42 Å, the older values being larger. This may be accounted for by the unsatisfactory method of calibration, for Sleator had to depend upon the value of the grating space and the measurement of an angle in the spectrometer, neither of which was reliable. However, if the average difference is subtracted from the older numbers, the variations seem to bear out Sleator's estimate of a probable error of 20 Å, for 25 successive differences are 62, 59, 63,

TABLE II

WAVE-LENGTHS AND WAVE NUMBERS OF LINES IN THE ABSORPTION BAND
AT 6.26 μ . THE ECHELETTE GRATING HAS 2880 LINES PER INCH
(A line whose relative intensity is 10 shows about 90 per cent absorption)

Line No.	Old No.	Rel. Int.	Wave No. per mm	Wave-Length (μ)	Line No.	Old No.	Rel. Int.	Wave No. per mm	Wave-Length (μ)
1.....		1	209.12	4.7819	51....	20	10	171.81	5.8204
2.....		1	206.61	4.8401	52.....		5	171.48	5.8316
3.....		2	204.34	4.8940	53.....		2	171.10	5.8447
4.....		2	201.85	4.9542	54.....	20'	6	170.58	5.8622
5.....		1	200.95	4.9763	55.....	21	10	170.08	5.8796
6.....	1	2	199.30	5.0176	56.....	21'	10	169.70	5.8928
7.....		1	198.91	5.0275	57.....		5	169.38	5.9039
8.....		1	197.56	5.0617	58.....		4	169.01	5.9168
9.....	2	2	196.80	5.0814	59.....	22	10	168.50	5.9349
10.....	3	1	196.20	5.0967	60.....		4	168.14	5.9473
11.....		1	195.57	5.1132	61.....	22'	5	167.59	5.9671
12.....		1	195.06	5.1266	62.....	23	7	167.01	5.9878
13.....		2	194.63	5.1377	63.....	24	4	166.37	6.0108
14.....	4	3	194.34	5.1456	64.....	25	10	165.43	6.0448
15.....		1	193.54	5.1669	65.....	26	10	164.79	6.0683
16.....	5	1	193.02	5.1807	66.....		8	163.81	6.1046
17.....		1	192.66	5.1905	67.....	27	10	163.65	6.1107
18.....	6	3	192.39	5.1978	68.....	27'	3	162.90	6.1388
19.....		3	191.90	5.2111	69.....	28	6	162.40	6.1576
20.....	7	2	190.98	5.2361	70.....	29	9	161.77	6.1816
21.....	7'	1	190.38	5.2527	71.....		1	161.39	6.1960
22.....	8	1	189.59	5.2745	72.....		2	161.03	6.2098
23.....	9	2	188.99	5.2914	73.....	30	1	160.78	6.2197
24.....	9'	1	188.55	5.3037	74.....	30'	2	160.36	6.2361
25.....		1	187.77	5.3256	75.....		1	160.17	6.2431
26.....	10	5	187.01	5.3474	76.....	31	2	159.56	6.2673
27.....		1	186.23	5.3696	77.....	31'	1	159.02	6.2887
28.....		1	185.88	5.3797	78.....		1	158.72	6.3006
29.....		1	185.40	5.3939	79.....	32	7	157.70	6.3413
30.....	11	5	184.52	5.4195	80.....	33	7	157.05	6.3675
31.....	11'	2	183.77	5.4416	81.....	33'	3	156.54	6.3881
32.....	12	4	183.02	5.4626	82.....	34	10	155.99	6.4105
33.....		4	182.60	5.4766	83.....		7	155.50	6.4309
34.....		1	181.84	5.4995	84.....	35	4	155.11	6.4472
35.....	13	3	181.15	5.5204	85.....		7	154.58	6.4690
36.....	13'	3	180.06	5.5537	86.....	36	10	154.07	6.4904
37.....		1	179.65	5.5665	87.....	37	8	153.45	6.5169
38.....	14	4	179.26	5.5785	88.....	38	7	152.82	6.5438
39.....		1	178.52	5.6016	89.....		7	152.61	6.5525
40.....	15	2	178.08	5.6154	90.....	39	10	152.23	6.5692
41.....	16	6	177.33	5.6392	91.....	40	8	151.80	6.5878
42.....		3	176.48	5.6666	92.....		4	151.27	6.6108
43.....	17	3	176.26	5.6735	93.....	41	10	150.79	6.6319
44.....	17'	3	175.82	5.6875	94.....		6	149.98	6.6675
45.....	18	5	175.00	5.7143	95.....	42	7	149.75	6.6778
46.....		1	174.43	5.7330	96.....	43	8	149.10	6.7069
47.....	18'	2	174.10	5.7439	97.....		5	148.77	6.7219
48.....	19	6	173.49	5.7641	98.....	44	2	148.23	6.7464
49.....		1	173.10	5.7771	99.....		4	147.78	6.7668
50.....		1	172.41	5.8003	100.....	45	8	147.39	6.7849

TABLE II—*Continued*

Line No.	Old No.	Rel. Int.	Wave No. per mm	Wave-Length (μ)	Line No.	Old No.	Rel. Int.	Wave No. per mm	Wave-Length (μ)
101....	46	7	146.60	6.8215	114....		6	139.55	7.1661
102....		10	145.82	6.8574	115....		6	138.80	7.2044
103....		2	145.29	6.8830	116....		3	138.33	7.2290
104....		5	144.87	6.9027	117....		1	137.83	7.2554
105....		1	144.35	6.9274	118....		4	137.47	7.2741
106....		8	143.76	6.9560	119....		3	136.93	7.3032
107....		1	143.34	6.9764	120....		4	136.35	7.3338
108....		3	143.08	6.9892	121....		1	135.55	7.3775
109....		4	142.41	7.0220	122....		5	134.00	7.4626
110....		7	141.96	7.0443	123....		2	133.71	7.4791
111....		2	141.14	7.0850	124....		2	131.94	7.5793
112....		4	140.55	7.1149	125....		2	131.31	7.6162
113....		5	140.00	7.1427	126....		1	130.11	7.6860

55, 46, 53, 46, 45, 54, 34, 46, 33, 25, 16, 38, 65, 45, 27, 31, 29, 36, 18, 34, 22, 31—all positive. Just one of the 59 wave-lengths is less than the later value, Number 16 in Table II; and one, Number 10, is very much (142 Å) greater. In these cases the former wave-length does not seem to represent the same line as the later one. If we consider now that Sleator plotted only one energy-curve at 6 μ , while the present values depend on three, and that the later method of calibration is much more precise, it seems fair to estimate the probable error of the wave-lengths in Table II as ± 4 Å.

It is plain that a refinement of analysis, which may cause two lines to appear where but one was listed before, is enough to make some of the wave-lengths appear quite wrong, while it may affect others not at all. In this connection it is to be noted that some of the lines of Figure 2 are sharp and definitely located, and appear to be the single effect of appropriate single causes. They may not prove to be separable into components, no matter what measure of resolution it becomes possible to apply. Such lines are numbers 38, 44, 61, 62, 68, 69, 70, 80, 81, and 101, for example. On the other hand, some of the so-called lines are probably complex, and their definite separation waits upon higher resolving power. Such are numbers 45, 51, 86, 93, and 102. It appears from this difference that some of the wave numbers in Table II represent radiation frequencies of definite significance in the process of light-absorption. They are valuable to as many significant figures as they may safely be carried. Other

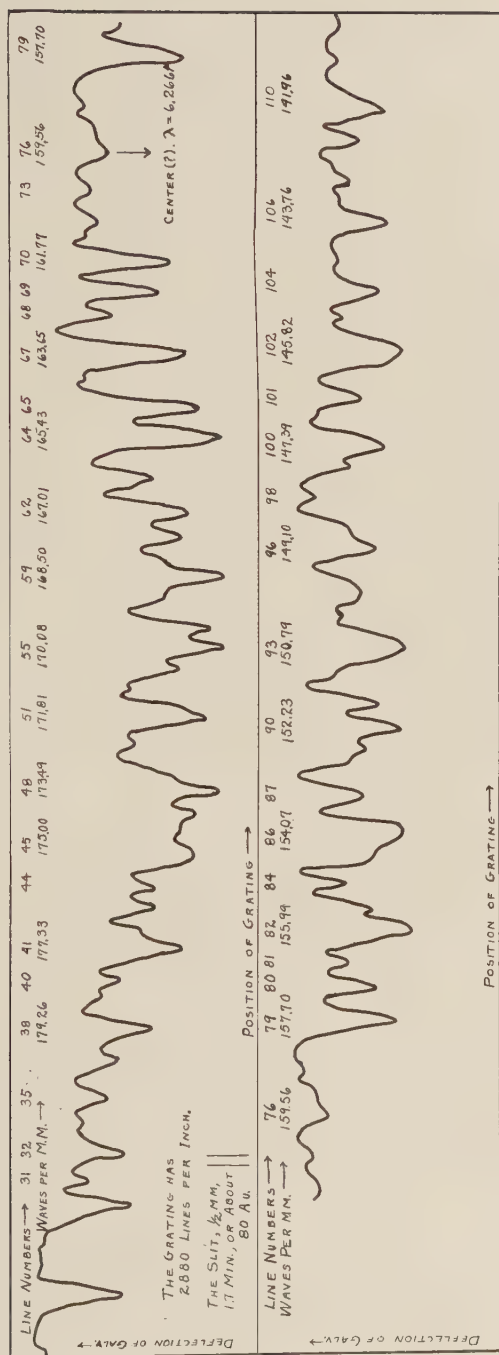


FIG. 2.—Part of the energy-curve, region of 6μ

wave numbers seem to be composite effects, representing no single transition in molecular state. It will probably be futile to base theoretical calculations on these numbers. In other words, not all the data of Table II are of equal interest or value. An examination of the graph will permit a decision upon the value to theoretical work of any particular number. There must, of course, be some systematic error in all these wave-lengths, for no one would claim to have determined the spectrometer constant with absolute precision, but the value used has been subject to so many checks and redeterminations by different observers that the probable error $\pm 4 \text{ \AA}$ seems to include variations on this account.

There is uncertainty about the significance of some of the measured lines in the actual process of absorption, but a certain degree of regularity is apparent in the curve of Figure 2. Lines 48, 51, 55, 59, 63, for example, occur at nearly equal intervals. This spacing suggests the diagram of Figure 3. The arrangement of Figure 3 with the co-ordinate axes rather than the graph inclined is a doubtful expedient for saving space. The equality apparent in the spacing along these lines may be fortuitous, but this is hardly likely. The three lines, however, have slightly different slopes, and, consequently, if one uses the formula $\Delta\nu = \frac{h}{4\pi^2 I}$ to calculate a moment of inertia, they indicate different values of I . The values appearing in the figure may not be real, for, if they are, a single corresponding change of state is related to absorption lines distributed among the whole set in no simple or obvious manner. It is, of course, impossible that there should be three principal moments of inertia represented by these numbers, and if they correspond simply to different stationary rotation states there should be more than three of them. Perhaps the two values closest together represent, in fact, a single one. At any rate, in the light supplied by our knowledge of the spectrum of hydrogen chloride, the expression $\frac{h}{4\pi^2 I}$ would appear to represent such a common frequency interval as Figure 2 most plainly shows. The fact mentioned above, that two wave numbers, though equally precise, may not be equally significant, must be taken into account in any theoretical consideration of these data.

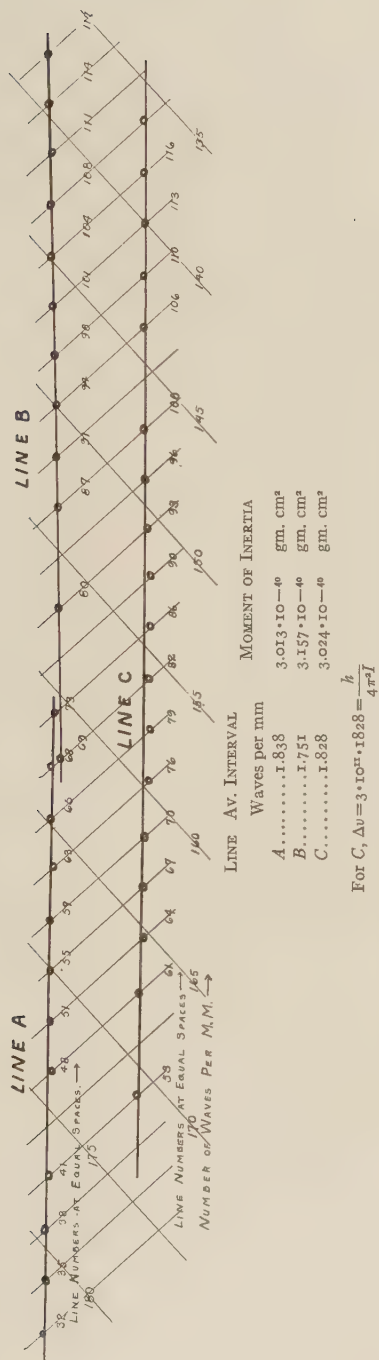


FIG. 3.—Linear relations between absorption lines, region near 6μ

The work in the second region to be considered represents the first application to the band near the wave-length 3.11μ of such high resolution as this apparatus permits, for Sleator's paper extended the band near 2.6μ to the line which he numbered 87 at 2.86μ , and he did not work any further toward longer waves. He supposed, in fact, that he had reached the end of the band. However, Hettner's map, in the paper already referred to on page 28, shows detailed absorption beyond the limit of Sleator's series. Also, in Hettner's paper on the band centers¹ the wave-length 3.15μ is of particular importance as it represents the octave of the "fundamental" at 6.26μ . The corresponding frequencies are Hettner's numbers ν_1 and $2\nu_1$.

This band was examined with a grating having 7200 lines per inch. The slits of the spectrometer were $\frac{1}{2}$ mm wide, which corresponded at the thermopile to about 32 Å. The calibration depended upon the wave-lengths of 10 lines in the spectrum of hydrogen chloride as given by Colby and Meyer (*loc. cit.* on p. 28). Figure 4 and Table III present the data obtained. Lines numbered 84, 85, 86, and 87 at the beginning of the table are those so numbered by Sleator. Of these four lines, the former wave-lengths average 4 Å (extremes 8 and -2) greater than present determinations, suggesting again a systematic error in the earlier calibration, decidedly smaller, however, than was made at 6μ . Leaving out of consideration the fact that the application of higher resolution may show part of these lines to be complex, and the present wave numbers accordingly meaningless, it may be estimated that the probable error in the wave-lengths is ± 2 Å.

It is interesting to compare Figure 3 with Hettner's map (*loc. cit.* on p. 28). In particular the center, if one may be guided by an appearance of symmetry, is near 3.11μ rather than at 3.15μ . In Figure 3 it may be noted also that the arrangement of lines is much less regular than in the other bands. In particular, one does not notice strong lines almost equally spaced, with weaker ones nearby on each side, which is an outstanding feature of the absorption near 6μ . The band near 3μ may accordingly depend upon a process or processes different from those which account for the others. It may, of course, represent a combination effect of common causes.

¹ G. Hettner, *Zeitschrift für Physik*, **1**, 345, 1920.

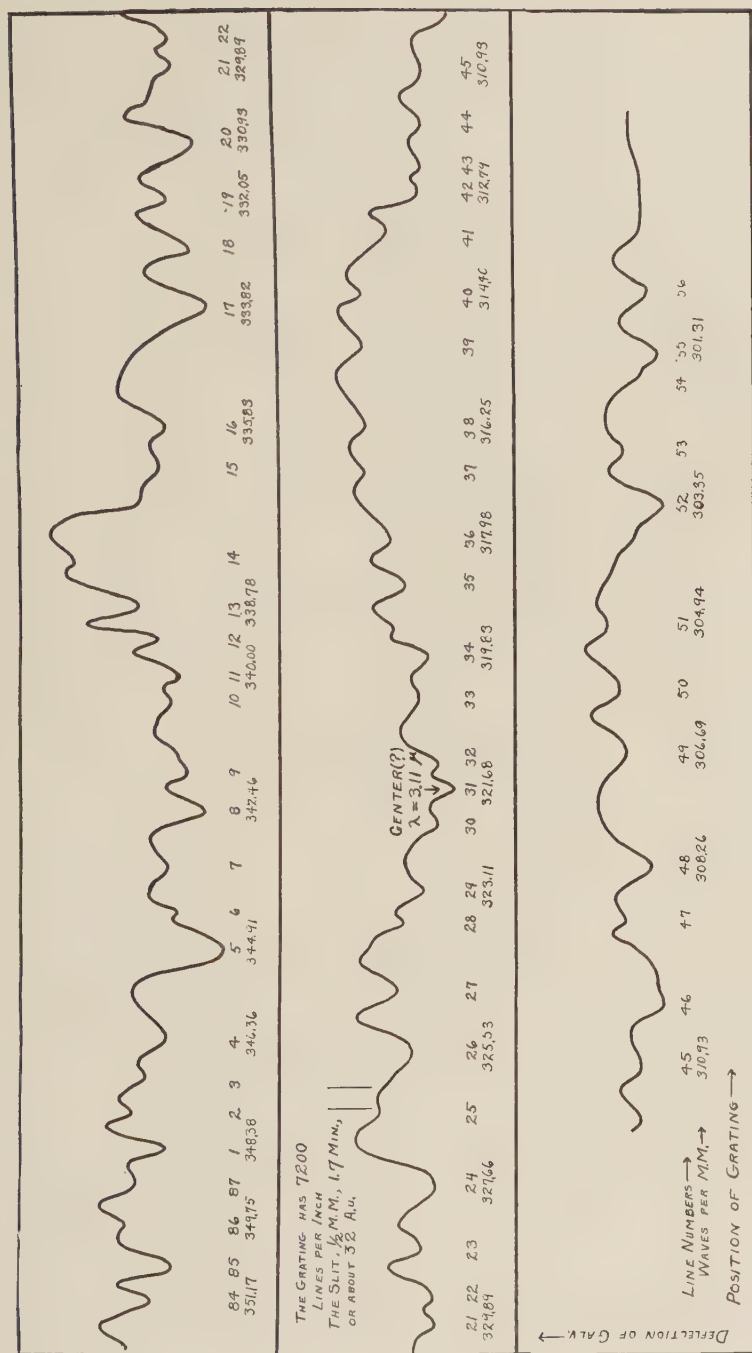


FIG. 4.—Energy curve, region of 3.15μ

The absorption band near 1.8μ seems to have a center at line 28, whose wave-length is 1.8700μ . This corresponds to Hettner's frequency $\nu_1 + \nu_2$, where ν_1 and ν_2 refer, respectively, to the bands at

TABLE III
WAVE-LENGTHS AND WAVE NUMBERS OF ABSORPTION LINES IN THE BAND
NEAR 3.11μ
(A line whose relative intensity is 10 shows about 20 per cent absorption)

Line No.	Rel. Int.	Wave No. per mm	Wave- Length (μ)	Line No.	Rel. Int.	Wave No. per mm	Wave- Length (μ)
84.....	9	351.17	2.8477	27.....	3	324.72	3.0796
85.....	10	350.46	2.8534	28.....	5	323.63	3.0900
86.....	3	349.75	2.8592	29.....	6	323.11	3.0949
87.....	4	349.02	2.8652	30.....	6	322.16	3.1041
1.....	8	348.38	2.8704	31.....	6	321.68	3.1087
2.....	2	347.71	2.8760	32.....	3	321.11	3.1142
3.....	3	347.03	2.8816	33.....	1	320.26	3.1225
4.....	5	346.36	2.8872	34.....	3	319.83	3.1267
5.....	10	344.91	2.8993	35.....	5	318.66	3.1383
6.....	3	343.95	2.9075	36.....	5	317.98	3.1449
7.....	3	343.20	2.9130	37.....	1	316.92	3.1554
8.....	8	342.46	2.9207	38.....	3	316.25	3.1621
9.....	2	341.62	2.9273	39.....	3	315.10	3.1739
10.....	3	340.39	2.9378	40.....	3	314.40	3.1806
11.....	5	340.00	2.9412	41.....	2	313.41	3.1907
12.....	5	339.53	2.9452	42.....	1	312.79	3.1971
13.....	6	338.78	2.9517	43.....	1	312.43	3.2007
14.....	2	337.93	2.9592	44.....	2	311.84	3.2068
15.....	3	336.56	2.9712	45.....	3	310.93	3.2162
16.....	3	335.83	2.9777	46.....	5	310.11	3.2247
17.....	4	333.82	2.9956	47.....	1	309.04	3.2359
18.....	5	332.93	3.0036	48.....	5	308.26	3.2440
19.....	3	332.05	3.0116	49.....	6	306.69	3.2607
20.....	3	330.93	3.0215	50.....	5	305.75	3.2706
21.....	5	329.89	3.0314	51.....	3	304.94	3.2794
22.....	4	329.39	3.0360	52.....	5	303.35	3.2966
23.....	1	328.55	3.0437	53.....	1	302.63	3.3044
24.....	5	327.66	3.0519	54.....	3	301.61	3.3155
25.....	2	326.54	3.0624	55.....	4	301.31	3.3188
26.....	2	325.53	3.0719	56.....	3	300.52	3.3276

6.26μ and 2.66μ . In this band Sleator located and measured 30 lines, and the map of Figure 5 and Table IV give values for 52. The values of λ given by Sleator are, except for two, larger than the present numbers, the differences being not greater than 11, nor less than -1, average difference 5.5 Å. The greatest differences (-1, 11, etc.) appear where the relative intensity of the lines is least, and where the present map shows more lines than Sleator could identify,

so perhaps the numbers compared really represent different things. However, there seems to be a systematic error in the former values of 4 or 5 Å, an amount by which they are too large. If this systematic difference be deducted from the earlier values, the extreme variation will be ± 5 Å between the earlier and later numbers, and it seems that the wave-lengths of Table IV should be affected by the probable error ± 2 Å, or even a little less.

The grating used for these numbers was the one employed by Sleator, having 15,000 lines per inch, without the characteristics of

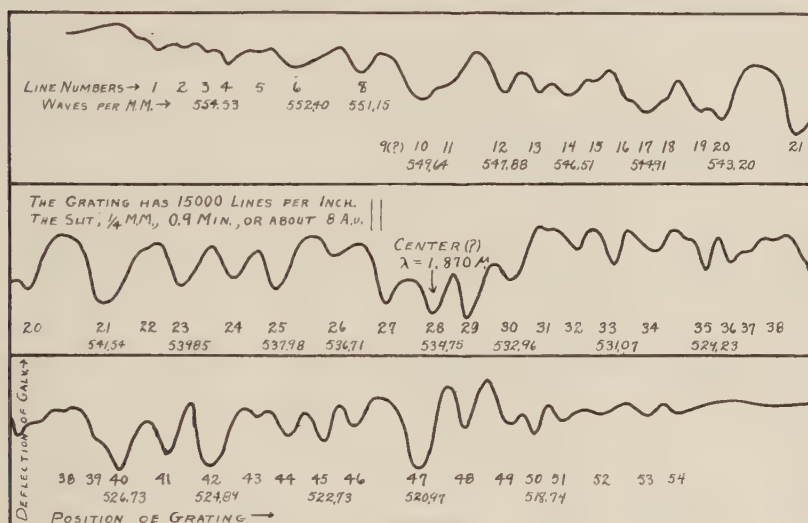


FIG. 5.—Energy-curve, region of 1.87μ

the echelette. The slit of the thermopile included a range of about 8 Å. If one compares the curve of Figure 5 with Figure 4 in Sleator's paper, it appears that the greater number of lines listed here is due largely to the confirmation of suggestions already noticeable in the earlier work but not at first considered reliable. The wave-lengths appearing here owe a somewhat greater accuracy to the better methods of measuring previously considered.

Such an improvement as has just been described has been made in the band at 1.3μ also. Here 28 lines have been measured. The use of a grating having 20,000 lines per inch accounts for the larger

number—Sleator lists 14 lines. The band at 1.3μ is, according to the present work, in about the same state of analysis as the band at 1.87μ was left by Sleator—a comparison of his Figure 4 with Figure 6 shows this similarity. It is a natural question whether these absorption regions actually possess the complex structure to be ob-

TABLE IV
WAVE-LENGTHS AND WAVE NUMBERS OF ABSORPTION LINES IN THE BAND
NEAR 1.87μ

(A line whose relative intensity is 10 shows about 35 per cent absorption)

Line No.	Rel. Int.	Wave No. per mm	Wave- Length (μ)	Line No.	Rel. Int.	Wave No. per mm	Wave- Length (μ)
1.....	1	555.51	1.8002	27.....	10	535.77	1.8665
2.....	2	555.04	1.8017	28.....	6	534.75	1.8700
3.....	1	554.53	1.8033	29.....	8	533.85	1.8732
4.....	2	553.89	1.8054	30.....	6	532.96	1.8763
5.....	1	553.25	1.8075	31.....	1	532.57	1.8777
6.....	3	552.40	1.8103	32.....	3	531.76	1.8805
7.....	1	551.89	1.8119	33.....	4	531.07	1.8830
8.....	5	551.15	1.8143	34.....	3	530.18	1.8861
9.....	1	550.25	1.8173	35.....	5	529.23	1.8895
10.....	9	549.64	1.8194	36.....	3	528.77	1.8912
11.....	5	549.17	1.8214	37.....	2	528.36	1.8927
12.....	6	547.88	1.8255	38.....	1	527.79	1.8947
13.....	4	547.13	1.8277	39.....	2	527.18	1.8969
14.....	3	546.51	1.8298	40.....	8	526.73	1.8985
15.....	1	545.90	1.8319	41.....	7	525.75	1.9020
16.....	2	545.36	1.8336	42.....	9	524.89	1.9052
17.....	9	544.91	1.8352	43.....	1	524.07	1.9081
18.....	8	544.42	1.8368	44.....	3	523.44	1.9104
19.....	7	543.69	1.8393	45.....	7	522.73	1.9130
20.....	10	543.20	1.8409	46.....	3	522.11	1.9153
21.....	10	541.54	1.8466	47.....	9	520.97	1.9195
22.....	1	540.70	1.8495	48.....	4	520.05	1.9229
23.....	7	539.85	1.8524	49.....	1	519.18	1.9261
24.....	7	538.86	1.8558	50.....	2	518.74	1.9277
25.....	9	537.98	1.8588	51.....	1	518.16	1.9299
26.....	4	536.71	1.8632	52.....	1	517.44	1.9326

served at 6μ , and what measure of similarity may ultimately be found in the details of the several bands. From the figures, the center at 6.26μ is seen to represent small absorption, while in the other bands a point of maximum absorption is evidently the center. However, some of these regions may, and others may not, contain lines of a zero branch. Also, nothing more than a doubtful appearance of symmetry has determined our choice of centers, so they may or may not represent points of special, or in different regions of the same,

physical significance. It may be noted that, compared to the whole extent of the band, the individual steps by which the analysis was made—the value of $\Delta\nu$ corresponding to one of the equal displace-

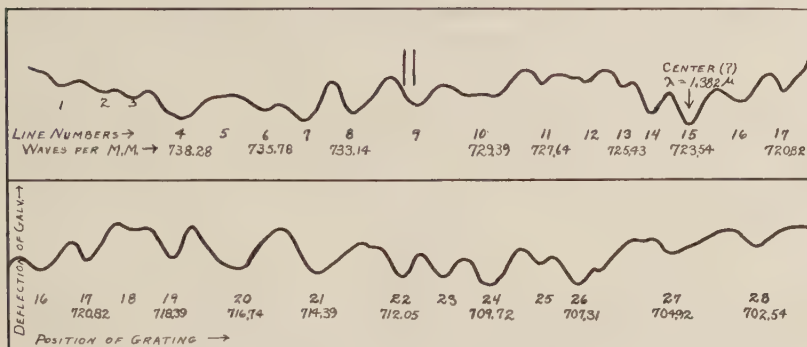


FIG. 6.—Energy-curve, region of 1.38μ . The grating has 20,000 lines per inch. The slit, $\frac{1}{4}$ mm, 0.8 min., or about 7 Å.

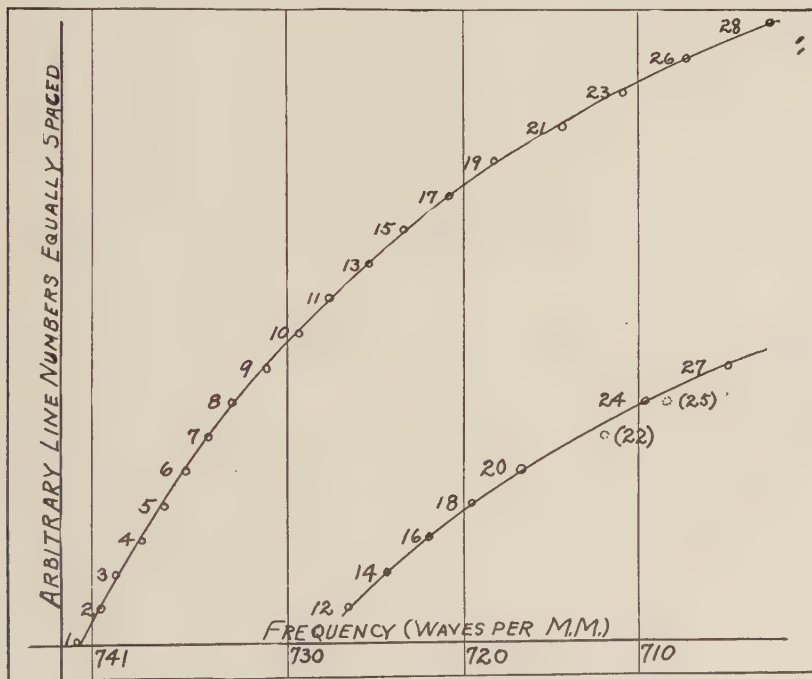


FIG. 7.—Regularities in the absorption band near 1.38μ

ments of the grating—is larger at 1.35μ than at 6.26μ . There is, accordingly, a more refined analysis of the latter band. The energy-curve itself appears in Figure 6 and the corresponding data in Table V. In Figure 7 appears the same sort of graph as in Figure 3. The wave numbers are plotted on one axis, and the arbitrary line numbers are equally spaced along the other. Here, however, the resulting lines are by no means straight, but have a form suggesting the distribution of absorption lines in the spectrum of hydrogen

TABLE V
WAVE-LENGTHS AND WAVE NUMBERS OF ABSORPTION LINES IN THE BAND
NEAR 1.38μ
(A line whose relative intensity is 10 shows about 25 per cent absorption)

Line No.	Rel. Int.	Wave No. per mm	Wave- Length (μ)	Line No.	Rel. Int.	Wave No. per mm	Wave- Length (μ)
1.....	2	741.84	1.3480	15.....	10	723.54	1.3821
2.....	1	740.52	1.3504	16.....	7	722.07	1.3849
3.....	1	739.64	1.3520	17.....	9	720.82	1.3873
4.....	7	738.28	1.3545	18.....	1	719.68	1.3895
5.....	1	736.92	1.3570	19.....	9	718.39	1.3920
6.....	5	735.78	1.3591	20.....	10	716.74	1.3952
7.....	9	734.48	1.3615	21.....	10	714.39	1.3998
8.....	10	733.14	1.3640	22.....	8	712.05	1.4044
9.....	9	731.26	1.3675	23.....	6	710.98	1.4065
10.....	6	729.39	1.3710	24.....	9	709.72	1.4090
11.....	2	727.64	1.3743	25.....	4	708.37	1.4117
12.....	1	726.59	1.3763	26.....	8	707.31	1.4138
13.....	3	725.43	1.3785	27.....	4	704.92	1.4186
14.....	7	724.53	1.3802	28.....	3	702.54	1.4234

chloride. Whether further analysis, if it becomes possible, will confirm or destroy this appearance of similarity it is impossible to say, but the regularity of the curves of Figure 7 can hardly be accidental. However, the intensities of the absorption lines vary in no systematic fashion along the series of Figure 7, which casts a doubt upon the importance of the alignment.

A comparison of these numbers with the table for the same region in Sleator's paper shows that the extreme differences in wave-length are 3 Å and -1 Å, average difference 1.4 Å, the former values being higher. This difference varies so little, and is so small, considering that the numbers were obtained by different observers with different gratings, that one seems justified in setting the prob-

able error of the wave-lengths in Table V as 1 Å. It does not seem likely that the same systematic error should remain in both calibrations.

It is possible now to compare the locations of the band centers as they are given by Hettner (*loc. cit.* on p. 38) with what appear to be the centers according to the data of this paper. The comparison appears in Table VI.

The first and third numbers in the second column do not agree as well as might be hoped with the observed values of the last col-

TABLE VI
LOCATION OF BAND CENTERS

Vibration Number	Wave-Lengths Computed from Data of This Paper for ν_1 and ν_2	Observed by Hettner and Others	Observed by Sleator and Phelps
ν_1		6.26 μ	6.2673 μ
ν_2		2.66	2.6720
$2\nu_1$	3.1337 μ	3.15	3.1087
$\nu_1 + \nu_2$	1.8733	1.87	1.8700
$2\nu_2$	1.3360	1.37	1.3821
$3\nu_1$	2.0891	2.00, 2.05	
$2\nu_1 + \nu_2$	1.4422	1.46	
$\nu_1 + 2\nu_2$	1.1013	1.13	
$3\nu_2$	0.8907		
$4\nu_1$	1.5535		
$3\nu_1 + \nu_2$	1.1724	1.16	
$2\nu_1 + 2\nu_2$	0.9367	0.94	
$\nu_1 + 3\nu_2$	0.7898	0.77	
$4\nu_2$	0.6680	0.69	

umn. Also the spectral region between the bands at 1.38 μ , 1.87 μ , and 2.67 μ was carefully examined during this work, and no absorption comparable in intensity with that at 1.38 μ could be found with the vapor normally present in the air, which sufficed to show the bands themselves. The lines listed as near 2.00 μ and 2.05 μ appear in the sun's spectrum, and are attributed to water.

Some interest attaches to a comparison of wave-lengths and frequencies of absorption lines in the near infra-red with those of lines in the far infra-red. Data for such a comparison appear in Figure 8, in which the absorption lines are represented along a scale of wave numbers. For those measured in the present study—that is, in the near infra-red region—the number actually plotted represents

one-half the difference between the wave numbers of the two lines of a pair in the band near $6\ \mu$. It must be noted that the correct location of the center of this band is by no means obvious, so that even what we call "a pair" may have no physical significance. We could only start near what appears to be the center and choose corresponding lines according to their spacing and appearance. In the case of lines nearest the center, the pairing seems from the curve to be real. The long lines of Figure 8 correspond to wave-lengths in the rotation spectrum as measured by Rubens and others.¹ These long lines occur in no regular order among the shorter ones representing the near infra-red. That is to say, the lines in the farther infra-red which make up the rotation spectrum have no obvious connection with what we have called the pairs in the band at $6.26\ \mu$. In this band, however, there are so many lines that one could, with the rotation spectrum in view, so choose the pairs that the long lines of Figure 8 would fall either on or near the short ones, or halfway between successive short ones. Such an arrangement would be of interest only if one were sure that the corresponding relation between near and far infra-red ought to exist, or if one found that the numbers of each pair, chosen with such a relation in mind, were really similar and similarly placed in the graph of Figure 2. With the great number of lines available at $6.26\ \mu$, one could find plausible indication of whatever relationship between near and far infra-red he wished to support.

It remains only to add that a great deal of work was done with absorption cells containing steam or carbon dioxide in order to check the actual responsibility of water for the absorption lines of the figures. In no case was a line enhanced by the tank of carbon dioxide, though it must have increased by a hundred fold the amount of that medium in the path of the radiation. The effect of the extra carbon dioxide was of particular importance near $1.38\ \mu$, for a harmonic of one of the strong bands near $2.8\ \mu$ might have been expected in this neighborhood. No indication of such a harmonic could be noticed.

With a tank of steam in the path, all the lines were more intense,

¹ H. Rubens, *Sitzungsberichte der Preussischen Akademie der Wissenschaften*, p. 3, 1921; p. 513, 1913. H. Rubens and G. Hettner, *ibid.*, p. 167, 1916.

on account, apparently, of the greater amount of water-vapor in the beam. Steam at various temperatures up to 350° C. was employed. The variation in temperature had no appreciable effect on the number, position, or relative intensity of the absorption lines. It might have been expected that a change of temperature would have shifted the maximum of absorption along the band, as is the case in the spectrum of hydrogen chloride, but no such effect could be observed.

UNIVERSITY OF MICHIGAN

October 1924

